# Searching for cryptoelectrons: Electron transfer reactions on insulating materials

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*Abstract* — **It is well known that high dielectric materials, such as polystyrene, demonstrate contact electrification. However, the mechanism by which these materials accumulate charge has been subject to extensive debate. Suggested mechanisms can be generalised into four main categories: electron transfer; ion transfer; material transfer; and the formation of mechanoradicals, but any permutation of the aforementioned mechanisms is also a possibility [1]. In our recent work, we have focused on exploring the proposed electron transfer model.**

**Utilising techniques developed for characterising nanodiamond surface functionalities [2] and inspired by the work of Liu and Bard [3], we have confirmed the presence of, and studied, redox chemistry on the surface of insulating materials via a combination of electrochemistry, spectroscopy and nanotechnology. More specifically, we have exploited the high surface area to volume ratio of nanoparticles to enable us to perform electrochemistry on these high energy surface sites (*e.g.* defects, edge planes, trapped electrons *etc.*) that exist on high band gap materials. Currently, we have determined the presence of, and characterised, such sites on nanodiamond particles ($d$ = 5-1000 nm), polystyrene particles ($d$ = 20-900 nm) and human hair fibres. Results demonstrate the presence of surface sites that are able to gain or lose electrons, unlike the bulk material itself. Such findings support the previously mentioned electron transfer mechanism for contact electrification.**

## I. INTRODUCTION

It is well known that the surface of dielectric materials can become charged when brought into contact with another material (*e.g.* a metal, semiconductor or other dielectric), both with or without mechanical agitation. Research into this topic is of significant interest as it has applications in a diverse range of economic sectors from mining to photocopying. Additionally, many industry's production lines are hindered by the presnece of electrostatic charging (most notably the electronics industry), and wish to eliminate it. Despite significant advancements in the understanding of contact electrification, the origin of its charge has long eluded scientists. Developments have, however, led to the proposal of several different mechanisms by which such charge separation can occur. These can be grouped into three main hypotheses, which are (1) electron transfer, (2) ion transfer and (3) material transfer [4]. Our research focuses on the former proposed theo-

ry, whereby electron transfer occurs between materials, and is responsible for the buildup and separation of charge.

Our research was inspired by the seminal work of Liu and Bard [3] that strongly reinforced the proposed electron transfer model. They demonstrated that redox reactions could occur at the surface of dielectric polymer materials, such as Teflon, polyamide and polymethylmethacrylate. Examples of said reactions include hydrogen evolution, metal deposition and electro-chemiluminescence. Expanding on their findings [3-6], and using techniques developed within our group [2], we proposed that if such redox reactions were occurring, one should be-able to observe them using electrochemical techniques. Here we report an overview of our methodologies with some of our main discoveries and observations. The full details of our work will be presented at the 2013 ESA meeting in Florida, and are also contained within a peer-reviewed paper on the electrochemistry of polystyrene nanospheres, which is to be published in due course [7].

## II. Experimental

### A. Equipment

All electrochemical experiments were carried out using a µAutolab PGSTAT potentiostat (Eco Chemie, Utrecht, Netherlands) running GPES (v4.9) via a standard three electrode setup. The working electrode was a boron-doped diamond disk ($d$ = 3.0 mm), press fitted into a Teflon body (Windsor Scientific, Slough, Unitied Kingdom). The counter electrode was fabricated in-house from platinum wire and sheet, cut into flags of approximately 4 cm$^2$. A stable reference potential was achieved by using an Ag/AgCl (sat. KCl) RE-5B reference half-cell (BASi, West Lafayette, America).

Mid-infrared spectra were recorded (50 scans) in attenuated total reflectance (ATR) mode using a Bruker Tensor 27 fourier transform infrared (FTIR) spectrophotometer (Bruker, Coventry, United Kingdom) fitted with a room temperature DLaTGS detector at 4 cm$^{-1}$ resolution. The Platinum ATR accessory consisted of a diamond prism operating with one reflection. Background spectra were collected prior to each experiment (100 scans).

Transmission electron micrograph (TEM) images were recorded using a Jeol 100 CX TEM with a 100 kV accelerating voltage. All nanoparticles were deposited from the experimentally prepared solution. Carbon coated copper TEM grids were used as the nanoparticle support.

Microscope images were captured using a Leica DMLM microscope with ×5, ×20 ×50 magnification lenses (Leica microsystems CMS GmbH,Wetzlar , Germany) using a Leica camera attachment and a Canon Powershot S70 camera.

X-ray photoelectron spectroscopy (XPS) was carried out with a Thermo K Alpha spectrometer using Al K alpha X-rays (1486.6 eV) with a spot size of 400 microns and a dual beam charge compensation system. The analyser was operated at pass energy of 200 eV for survey spectra (consisting of 10 scans) and 50 eV for high resolution core line measurements (consisting of 20 scans). XPS operation and spectrum analysis was performed using Thermo Avantage software (version 5.41).

## B. Chemicals

Latex beads, polystyrene (0.8 µm mean particle size), potassium dihydrogen phosphate (>98%), potassium phosphate dibasic (puriss, >99%) and potassium hexachloroiridate(IV) were all purchased from Sigma-Aldrich (Dorset, England). All solutions were prepared from water obtained from a Millipore Milli-Q Gradient A10 water filter (18.2 M Ω). Electrodes were cleaned by mechanical polishing with MasterPrep alumina polishing suspension, 0.05 µm (Buehler, Dūsseldorf, Germany) and deionized water using 2-7/8" microcloth polishing pads (Buehler, Dūsseldorf, Germany).

## C. Drop coating method

As received PS-[SO$_4$]$^{2-}$ suspensions contained surfactants and inorganic salts as stabilising agents. These were removed prior to drop-coating and performing electrochemical and spectroscopic experiments. Briefly, PS-[SO4]$^{2-}$ suspension (50 µl) was added to doubly deionised water (1 ml) in an Eppendorf tube and shaken until homogenous. The diluted suspension was then centrifuged at 6,000 rpm for 12 min, causing the PS-[SO$_4$]$^{2-}$ beads to pellet at the bottom of the vial. Most of the water was then carefully removed and replaced with clean doubly deionised water (1 ml). This procedure was repeated three times. After the final centrifuge, fresh doubly deionised water (1 ml) was added and the suspension left overnight.

Clean, dry electrodes were drop-coated with the purified PS bead suspension (1 µl) and left to dry in air for 15 min to produce a PS coated electrode. This procedure is outlined in Figure 1.
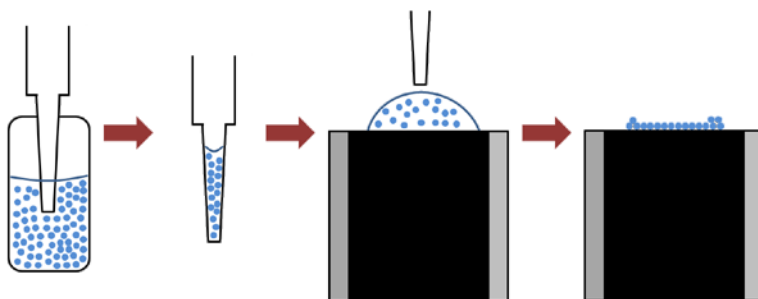


Fig 1. Illustration of the drop coating technique used to deposit polystyrene nanospheres onto an electrodes surface. This method gives very repeatable and reproducible surface areas and spreading patterns.

## D. Agitation studies

The effect of various agitation treatments on the amount of surface redox species observed was also investigated. For these experiments, the initial cleaning step was changed to dialysis, as this allowed soluble additives to be removed whilst limiting the amount of agitation to the polystyrene nanospheres. The membrane was a pre-treated standard grade, regenerated cellulose dialysis membrane (Spectrum Laboratories), with a molecular weight cut off of 3,500 Da and a flat width of 45 mm. Membranes were received in an aqueous solution containing sodium azide preservative (0.05 %), which was

removed by dialysis against distilled water for 2 h. Dialysis of the polystyrene solution (diluted tenfold from the commercial stock solution) was subsequently performed against distilled water for 48 h (changing the water every 12 h). It was from this cleaned suspension that the additional agitation treatments were performed (*i.e.* centrifugation and sonication), and subsequently, their electrochemical activity and spectroscopic properties recorded and analyzed.

## E.  *Electrochemical measurements*

Cyclic voltammetry experiments were performed on the PS-$[SO_4]^{2-}$ nanoparticle coated electrodes. Different applied potential windows (0.0 V → $0.4 \leq E_{max} \geq 1.0$ V) and a range of pH environments (4-9) were studied (all at 20 mV s$^{-1}$ unless otherwise stated). The pH of the electrolyte solution was controlled using different ratios of dipotassium hydrogen phosphate and potassium dihydrogen phosphate buffer solutions ($[c] = 0.1$ M). Prior to coating with the PS-$[SO_4]^{2-}$, BDD electrodes were polished, cycled for 3 scans (0.0 → 1.0 → 0.0 V, at 20 mV s$^{-1}$), and rinsed with deionised water. This procedure was repeated twice to ensure a stable background response was observed. The electrode was then drop-coated with PS-$[SO_4]^{2-}$ nanoparticles (via the procedure outlined previously), immersed into the electrolyte solution, and scanned three times. Upon completion of the final scan, the PS-coated electrode was immediately polished to remove the polystyrene nanospheres.

## F.  *Spectroscopy*

The effect of chemical and electrochemical oxidation on the surface functionality of the polystyrene nanoparticles was studied using ATR-FTIR spectroscopy and XPS. ATR-FTIR spectra were collected by drop-coating the polystyrene nanoparticles (in an identical manner to the electrochemical experiments) onto the diamond prism. Spectra of the oxidized polystyrene nanoparticles was achieved by treating a polystyrene suspension with potassium hexachloroiridate(IV) for 30 min, and subsequently removing the oxidising agent in a similar manner to that of the stabilising agent removal (see drop coating method section). XPS was performed on pure powder samples that were obtained by pelleting the polystyrene suspensions by centrifugation and carefully removing as much solution as possible (via pipette), before drying *in vacuo* for 48 h.

### III.  Results and Discussion

Polystyrene nanospheres were not the first dielectric material (that we discovered) to display surface redox activity [2]. However, we chose polystyrene for our primary study due to its low cost, availability, and excellent synthetic reproducibility. Each nanosphere is virtually identical, which not only is important experimentally, but simplifies modeling experimental observations considerably. A TEM and optical micrograph of drop-cast polystyrene nanospheres on a BDD electrode are shown in in Fig. 2.
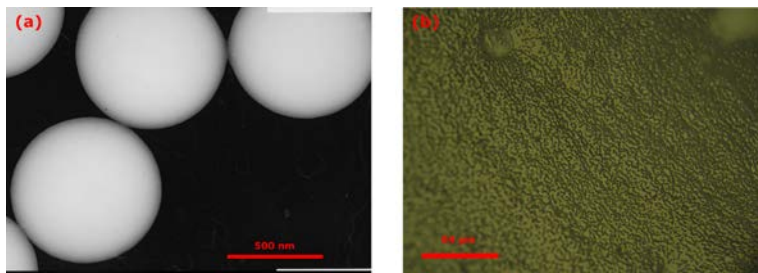
Fig 2. (a) A TEM micrograph and (b) an optical photograph of a polystyrene drop-cast film on a carbon coated TEM copper grid and a BDD electrode respectively.

Polystyrene nanosphere coated electrodes (fabricated as described in the experimental section) were initially studied in pH 6 phosphate buffer. An example of this voltammetry is shown in Fig. 3. The first scan of the experiment is shown in the left frame (a), where the second scan is shown in the right frame (b).

As can be seen upon analyzing the data there are two separate redox phenomena occurring. Firstly, the polystyrene undergoes an oxidation at *circa*. +0.725 V. Secondly, a new redox couple appears on the second scan at *circa*. +0.285 V. These experiments were carefully repeated many times, both with and without the presence of polystyrene, and it can be said with good certainty that these redox peaks are due to electron transfer reactions occurring on the polystyrene nanospheres. The emergence of a redox couple at +0.285 V occurs only if the beads are previously subject to potentials greater than +0.6 V (*i.e.* if they first undergo the oxidation at +0.725 V). This suggests that there are active sites on the nanosphere surface that once oxidized (irreversibly), are converted to a new species with reversible electrochemistry at a lower formal potential. The scan rate and pH dependence of these peaks has been investigated, the results of which are contained elsewhere [7].
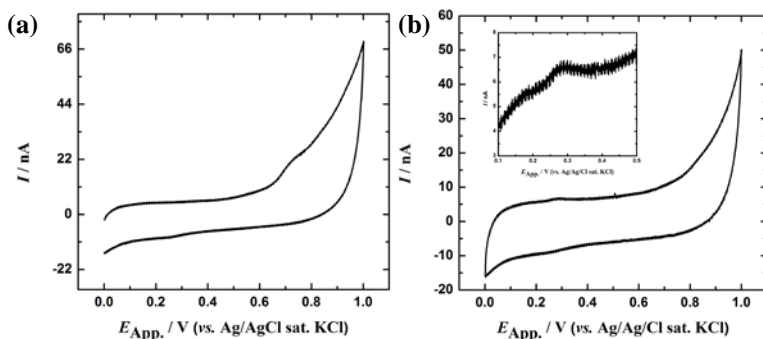


Fig 3. Voltammetry of a polystyrene nanosphere coated BDD electrode ($d = 3$ mm). (a) First scan, where an oxidation peak is observed at *circa*. +0.725 V, (b) second scan, a new redox couple is observed at *circa*. +0.285 V. The insert is a magnification of the potential region where the new redox couple is present. The scan rate was 20 mV s$^{-1}$.

In order to determine what chemistry is occurring at the nanosphere surface we employed FTIR and XPS spectroscopic techniques. However, due to experimental challenges that occur when working directly with coated electrodes, we carefully selected a chemical oxidizing agent to replace the electrochemical oxidation (potassium hexachloroiridate(IV), $K_2IrCl_6$). Polystyrene nanosphere suspensions were treated with $K_2IrCl_6$ (20 μM) in aqueous solution for 30 min before removing the species (by following the same procedure outline for the removal of preservatives and stabilizers). The liquid was then either drop-cast, (FTIR measurement) or removed by evaporation, *in vacuo*, and the resulting solid analyzed (XPS). Fig 4. shows pre-treatment (filled-black curve) and post-treatment (red line) ATR-FTIR spectra. The visible black areas signify a loss at that wave number. Key peaks changes and their corresponding vibrations, are shown in Table 1 [8].

FTIR evidence, coupled with data obtained via XPS [7], indicates that upon oxidation a phenolic species is formed. This leads to the conclusion that the new redox couple is potentially a quinone/hydroquinone species. Comparing literature values for phenol formation [9-10] and quinone electrochemistry [10-11] reinforce this hypothesis, as they both occur around the corresponding potential values.
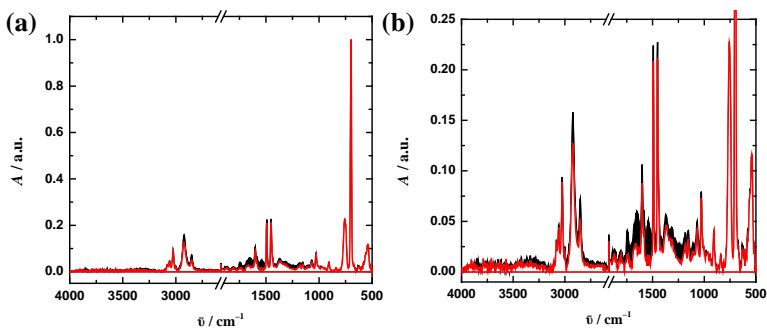


Fig 4. (a) FTIR of polystyrene nanospheres (black filled line) and $K_2IrCl_6$ treatment polystyrene (red line). (b) Magnification of the same figure. The spectra were properly normalized in order to directly compare samples, and remove any concentration effects.

Table 1: A table containing the key differences observed between the pre and post $K_2IrCl_6$ treated polystyrene nanosphere ATR-FTIR spectra (Fig 4.). Pink highlighting signifies an increase in signal at that wavenumber, whereas blue highlighting signifies a decrease in signal at the corresponding wavenumber.

| $\Delta\bar{v}$ / cm$^{-1}$ | Functionality |
|---|---|
| ↑3032 | **C-H** aromatic stretch due to **C-H** contraction at $C_2$ and $C_6$ and extension at $C_3$ and $C_5$ |
| ↓3060/3024 | Aromatic stretch due to **C-H** at the $C_2$ and/or $C_6$. |
| ↓2922/2847 | **C-H** (CH$_2$) asymmetric and symmetric stretches |
| ↓1773 | Overtone band ($v_{10A} + v_{17A}$) and slight red-shift |
| ↓1742/1640/1535 | Overtone band ($v_{10A} + v_{17B}$, $v_{10B} + v_{17B}$ and $v_{11} + v_{10A}$) |
| ↑1493/1448 | Fundamental ring stretching mode and overtone band ($v_{19A}(A_1)$; $v_4 + v_{10A}$) |
| ↑1358/1339 | **C-H** aromatic stretch and overtone band ($v_5 + v_{16A}$) |
| ↓1240 | Overtone band ($v_{10A} + v_{16A}$) |
| ↑1026 | Fundamental ring stretching mode ($v_{18A}(B_2)$) |
| ↑944 | Overtone band ($v_4 + v_{16A}$) |
| ↑907 | Fundamental ring stretching mode ($v_{17B}(A_1)$) |
| ↑785/699 | Fundamental ring stretching mode ($v_{10B}(B_2)$ and $v_{11}(B_2)$), blue shifted (possibly due to *ortho* substitution or oxidation of $\alpha$-carbon *w.r.t* to phenyl ring) |
| ↑568/537 | Fundamental ring stretching mode ($v_{6A}(A_1)$), red shifted (possibly due to *para* substitution) and ($v_4$ ($B_2$)) |

Thus far we have focused on identifying surface sites that can undergo electron transfer reactions. Having identified such species it is important to ascertain how they are formed or activated and since contact electrification requires, at the very least the coming together of two systems, we investigated the effect different agitation techniques had on the amount of electron transfer observed. Similar studies have been performed at a larger particle size, one example of which is the work carried out by Grzybowski B.A. *et al.* [12]. Fig 5. shows a preliminary study on the difference in measured charge between polystyrene nanospheres subject to minimal mechanical interactions (dialysis cleaned), and then the same sample batch after centrifugation (a more aggressive agitation technique).
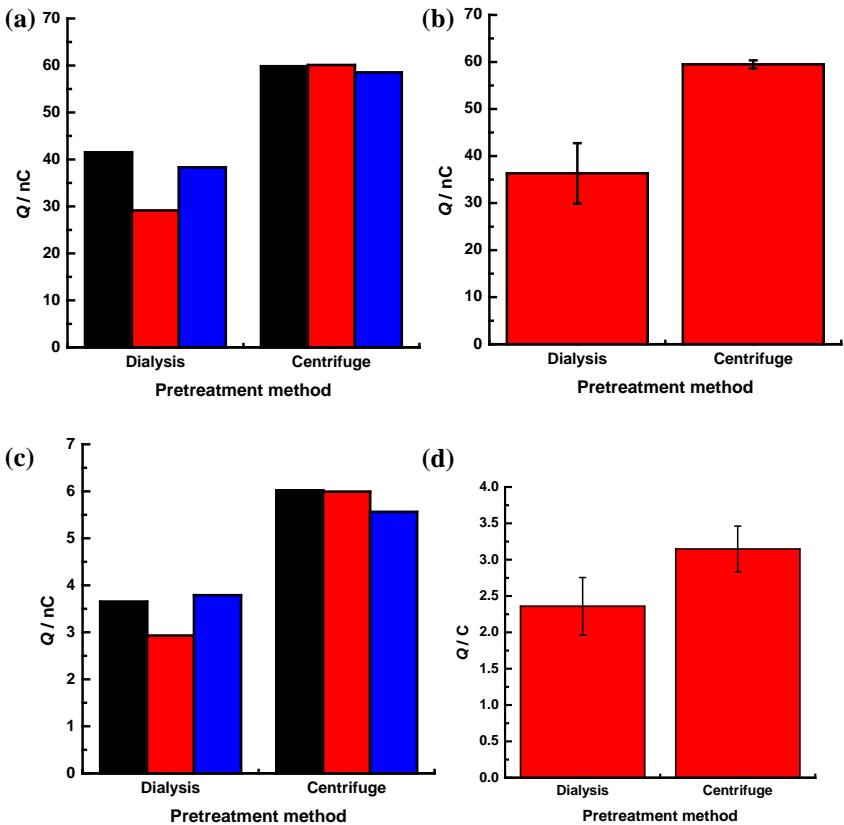
Fig 5. (a) $Q$ vs. pre-treatment type (sample set size = 3) of the oxidation process observed on the first cycle ($E_p \approx$ 0.725 V) and (b) the statistical analysis of these data (mean with standard deviation error bars) of this peak. (c) $Q$ vs. pre-treatment type (sample set size = 3) of the oxidation process observed on the second, and subsequent cycles ($E_p \approx 0.285$ V) and (d) the statistical analysis of these data (mean with standard deviation error bars) of this peak.

Our preliminary studies showed that increasing the extent of agitation the nanospheres are subjected to, with each other or the container walls, increased the amount of electron transfer observed. This logical discovery led to extending this study by increasing the sample set size (from 3 to 10), and adding another agitation technique (sonication) [7].

In addition to our findings regarding the study of the dielectric material polystyrene, here we present an experimental and analysis methodology that can be used to study any dielectric material and determine the presence of redox active surface sites, *i.e.* cryptoelectrons. The detection of such species, even at low surface concentrations is made possible due to the careful choice of material size, exploiting the surface area to volume ratio of nanoparticles, and equipment, specifically the low background capacitance and large voltage window that is exhibited by boron-doped diamond electrodes.

## IV. Conclusion

We have shown that dielectric materials (*i.e.* polystyrene, diamond and keratin) have redox active surface groups that can be modified and detected via electrochemical and spectroscopic means. Furthermore, we have demonstrated that the amount of redox active groups on the materials surface is dependent on the mechanical agitation history of the species. These findings suggest that contact electrification could plausibly occur via an electron transfer mechanism, occurring between high-energy surface sites, and are in agreement with the findings of Liu and Bard [3-6]. The observation that more aggressive agitation produces a greater number of observable sites highlights this is a mechanically activated process.

Further work is required to ascertain whether it is these cryptoelectrons sites that are directly responsible for charge separation that occurs in contact electrification (tribocharging) on all size scales, either completely or in part (via a combination of mechanism). Additional studies are also required to confirm our current proposed mechanism for polystyrene redox surface chemistry. Such findings should have a great impact on society's use of electrostatics by, for example, providing the ability to specifically induce, inhibit and control electrostatic charging, as well as allowing researchers to obtain useful information about active surface sites on dielectric materials such as the HOMO/LUMO energies for cryptoelectrons. Further investigations into the intensity and exposure time of agitation would also prove an interesting, and no doubt, fruitful study.

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